Chapter 8

Solid Materials

1. **What is a unit cell?**
   A unit cell is the smallest repeat unit of the crystal.

3. **How many unit cells are shown in Figure 8.17b?**
   Figure 8.17b is eight unit cells. A yellow sphere is at the center of each unit cell.

5. **What is the Fermi level?**
   The Fermi level is the energy of the occupied orbital that has the greatest energy.

7. **What is a band gap?**
   The band gap is the energy separation between the valence and conduction bands.

9. **The band structures of a conductor, a semiconductor and an insulator are shown to the right. Identify each.**
   A has the largest band gap, so it is the insulator. B has a partially filled band and is a metallic conductor.
   C is the semiconductor because its band gap is less than that of A.

11. **Gold crystallizes in a face-centered cubic geometry that is 4.08 Å on each side.**
   a, **Draw a picure showing the face of the unit cell.** See Figure 8.4b in the text.
   What atomic radius of gold is required for this geometry?
   Use Equation 8.1b for fcc unit cells and the given value of a, $r = \frac{\sqrt{2}a}{4} = \frac{\sqrt{2}\times 4.08}{4} = 1.44\ \mathring{A}$

   b. **How many gold atoms are present in the unit cell?** fcc unit cells have 4 atoms.

   c. **What is the volume of the unit cell in Å^3?** $V_{cell} = a^3 = 4.08^3 = 67.9\ \text{Å}^3$

   d. **What is the volume occupied by the atoms in the unit cell?**
   Volume of one atom = $\frac{4}{3}\pi r^3 = \frac{4}{3}\pi(1.44^3) = 12.5$ Å; Volume of four atoms = $V_{atoms} = 4 \times 12.5 = 50.0$ Å

   e. **Based on your results to c and d. what is the packing efficiency of the unit cell? How does this compare with the packing efficiency expected for a fcc unit cell?**
   $PE = \frac{V_{atoms}}{V_{cell}} \times 100\% = \frac{50.0}{67.9} \times 100\ \% = 73.6\%$, which is the packing efficiency for a fcc unit cell

13. **A compound formed between calcium, titanium, and oxygen crystallizes in the perovskite structure shown in the margin. Ca^{2+} cations (green spheres) reside on the corners of the unit cell, the Ti^{4+} cation (blue sphere) resides in the body center of the cubic cell, and O^{2-} anions (red spheres) reside on each of the cell faces. What is the formula of the compound?**
   Ca^{2+} ions reside on the corners: 8 corners × $^1/_8$ Ca^{2+} / corner = 1 Ca^{2+} ion
   Ti^{2+} ion resides in the body center: 1 body center × 1 Ti^{2+} / body center = 1 Ti^{2+} ion
   O^{2-} ions reside in the face centers: 6 face centers × ½ O^{2-} / face center = 3 O^{2-} ions
   Formula = $CaTiO_3$

15. **Calculate the atomic radius and density of copper if it crystallizes in a fcc unit cell that is 3.61 Å on a side.**
   $fd^2 = 3.61^2 + 3.61^2 = 26.1\mathring{A}$; $fd = 5.11\mathring{A} = 4r$; $r = \frac{5.11}{4} = 1.28\mathring{A}$

   $$d = \frac{m}{V} = \frac{\left(\frac{4}{6.02\times10^{23}}\text{ mol}\right)\left(\frac{63.5\text{g}}{\text{mol}}\right)}{(3.61\times10^{-8}\text{cm})^3} = \frac{4.22\times10^{-22}\text{g}}{4.70\times10^{-23}\text{cm}^3} = 8.97\text{ g/cm}^3$$

17. **How does the cesium chloride structure differ from a body-centered-cubic structure?**
   In a body-centered-cubic structure, the species in the center is the same as those on the corners. Cs^{1+} occupies one site, but Cl^{1-} ions occupy the other, so CsCl is not body-centered-cubic.

19. **Use the method employed in Example 8.4 to calculate the packing efficiency of a simple cubic unit cell.**
   There is only one atom in a simple cubic unit cell. Substitute into the PE equation in Example 8.4

   $$PE = \frac{1(\frac{4}{3})\pi r^3}{(2r)^3} \times 100\% = \frac{4.2}{8} \times 100\% = 52\%$$

21. Consider the structure of CsCl shown in Figure 8.15a.

a) Along which line (edge, face diagonal, or body diagonal) do the ions touch? edge

b) Use the ionic radii in Table 8.3 to determine the edge length of the unit cell.

$a = 2r_{Cat} + 2r_{An} = 2(r_{Cat} + r_{An}) = 2(1.81 + 1.67) = 6.96$ A $= 6.96\text{x}10^{-8}$ cm

c) What is the volume of the unit cell? $V_{UC} = a^3 = (6.96\text{x}10^{-8}\text{ cm})^3 = 3.37\text{x}10^{-22}\text{ cm}^3$

d) What is the volume occupied by the ions?

V_{Cat} = (4 cations)$(^4/_3\pi)r_{Cat}^3 = (4)(^4/_3\pi)(1.81\text{x}10^{-8}\text{ cm})^3 = 9.93\text{x}10^{-23}\text{ cm}^3$

V_{An} = (4 anions)$(^4/_3\pi)r_{An}^3 = (4)(^4/_3\pi)(1.67\text{x}10^{-8}\text{ cm})^3 = 7.80\text{x}10^{-23}\text{ cm}^3$

$V_{Ions} = V_{Cat} + V_{an} = 9.93\text{x}10^{-23} + 7.80\text{x}10^{-23} = 1.77\text{x}10^{-22}\text{ cm}^3$

e) What is the packing efficiency of the unit cell? How does this packing efficiency compare to that of a simple cubic unit cell?

$$PE = \frac{V_{Ions}}{V_{UC}}\times 100\% = \frac{1.77\times 10^{-23}}{3.37\times 10^{-23}}\times 100 = 52.5\%$$ same as a simple cubic unit cell

$$PE = \frac{V_{Ions}}{V_{UC}}\times 100\% = \frac{4.43\times 10^{-22}\text{ cm}^3}{6.50\times 10^{-22}\text{ cm}^3}\times 100\% = 68.2\%$$ same as a bcc

23. Explain at the molecular level why graphite can be used as a lubricant but diamond cannot.

The covalent bonds in graphite are in a plane while the planes interact through dispersion forces. The dispersion forces are weak and the planes slide freely over one another making graphite a lubricant. In diamond, the covalent bonding is three-dimensional and there are no weak interactions.

25. Describe nanotubes and explain why they are important. How is the structure of a nanotube related to that of graphite?

Nanotubes are cylinders of carbon. Their structure can be viewed as a sheet of graphite that has been rolled into a cylinder. They are metallic conductors or semiconductors depending on how the sheet is rolled. They have been used as molecular wires and in the construction of transistors and logic devices. They are important building blocks in the new field of molecular electronics.

27. What are clays? Why do some clays swell in the presence of water while others do not?

Clays are also composed of Al, Mg, and/or Fe and Si and O. They are two dimensional layered structures. In one type of clay (kaolinite), the layers hydrogen bond, which reduces the space between the layers. Kaolinites do not swell because water cannot get between the layers. In smectic clays, the hydrogen bonding sites are burried within the layers, so there is no hydrogen bonding between layers. Consequently the layers are farther apart and water can get in between the layers, which causes the clay to swell.

29. Indicate the substance with the higher melting point in each pair. Explain your choice.

a. CsBr or AlN

The force of attraction of two ions depends on the product of the charges on the ions. Therefore, the force of attraction between an Al^{3+} ion and a N^{3-} ion is greater than that between a Cs^{1+} ion and a Br^{1-} ion. Consequently, AlN has the higher melting point.

b. CaF_2 or CS_2

CaF_2 is ionic while CS_2 is molecular. Ionic bonds must be broken in order to melt an ionic solid while only relatively weak dispersion forces must be overcome to melt CS_2. CaF_2 has a much higher melting point. CaF_2 is a solid at room conditions while CS_2 is a liquid.

c. H_2S or ZnS

ZnS (zinc blende) is a covalent solid in which covalent bonds must be broken in the melting process. H_2S is a molecular substance in which only dispersion forces and weak dipole-dipole forces must be overcome in the melting process. ZnS has a much higher melting point and is a solid at room conditions while H_2S is a gas.

31. Each of the following substances is a solid at room temperature. Indicate whether each is a molecular, metallic, ionic, or covalent solid.

a) Si covalent solid **b) Ag** metallic **c) I_2** molecular